I. E. Cooper

A Study of the Methods of Extracting Beryllia From Beryl

A STUDY OF THE METHODS
OF
EXTRACTING BERYLLIA FROM BERYL

BY

ISADORE EARL COOPER

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

ISADORE EARL COOPER

ENTITLED A STUDY OF THE METHODS OF EXTRACTING

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IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE

B S Hopkins.
Instructor in Charge

APPROVED: Geo D Beal

HEAD OF DEPARTMENT OF Chemistry

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INTRODUCTION

I Acknowledgment

The writer takes this opportunity to thank Professor B. S. Hopkins, who directed this work, not only for the invaluable suggestions, aid, advice, and encouragement proffered, but also for his services in promoting the spirit of research in his students. Thanks are also due Professor D. F. McFarland for placing at the writer's disposal the apparatus and equipment of the industrial division and for his helpful suggestions regarding operations on a large scale.

II Object

The purpose of the investigation was to study those methods of extracting beryllium oxide from beryl that promised to be successful on a large laboratory scale. The plan was to prepare the compound by several methods on a small scale, and then to pick out those which worked best and try them on a larger scale.

One of the reasons that beryllium is still a "rare" element, although there are adequate deposits of its minerals, is the difficulty of obtaining it in a form free from aluminum and iron[2,8]. The most important compound is the oxide because it finds use in incandescent mantles, spark plugs, abrasives, and as a catalytic agent for the

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condensation of certain esters[12,17]. The oxide is the starting point for the preparation of the other compounds of beryllium as well as the metal.

III Historical and Theoretical

While attempting to prove the chemical identity of the emerald and beryl in 1797, L. N. Vauquelin discovered that a portion of the precipitate which had previously been supposed to be aluminum hydroxide was thrown out of its solution in potassium hydroxide on boiling. He investigated this new hydroxide and found that it was soluble in ammonium carbonate and formed no alum. These observations led him to announce in 1798 the discovery of the oxide of a new element, and called the oxide "the earth of beryl".[19]

In the next few years Vauquelin made other compounds of beryllium; among which were the sulphate, nitrate, chloride, phosphate, carbonate, citrate, tartrate, and acetate in impure form[20].

Since Vauquelin many investigators have proposed different methods for the preparation of the oxide. Those which seemed most satisfactory are reviewed below.

The method invented by Gibson is based on the principle that ammonium hydrogen fluoride effects the complete decomposition of beryl at a relatively low temperature, even when the mineral is only coarsely ground[6]. A large amount of the silica is removed as volatile ammonium fluosilicate, while the metals form soluble fluorides. These are converted to the sulphates and the beryllium separated by solution in ammonium carbonate.

Lebeau gets the mineral into solution by a fusion with calcium fluoride, and treatment of the powdered melt with sulphuric acid[11].

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The acid converts the aluminum, beryllium, iron and calcium to sulphates, and liberates the silica as silicon fluoride. To the solution of the sulphates, potassium carbonate is added to neutralize the excess acid. On evaporation, most of the aluminum is removed as potassium aluminum sulphate. The beryllium is separated by means of its solubility in ammonium carbonate and precipitation from that solution on boiling.

Pollok fuses the beryl with caustic soda, dissolves the resulting mass in hydrochloric acid, precipitates with ammonium hydroxide and redissolves the precipitate in hydrochloric acid[16]. By saturation of this solution with hydrogen chloride, nearly all of the aluminum is precipitated as the tetra hydrated chloride. The beryllium is recovered by its solubility in ammonium carbonate.

Parsons fuses the mineral with potassium hydroxide, dissolves the product in sulphuric acid and evaporates to dryness to remove the silica[14]. The soluble aluminum, potassium, beryllium and iron salts are extracted by means of hot water. Most of the aluminum is separated as potassium alum, while the rest of the aluminum and iron are removed by a concentrated sodium bicarbonate solution. The beryllium is obtained by diluting the sodium bicarbonate solution and heating.

The method proposed by Copaux is based on the fact that sodium fluosilicate is decomposed at about 750 degrees C. into sodium fluoride and silicon fluoride, a very active gas which at about 850 degrees C. decomposes beryl with the formation of sodium fluorberyllate and sodium fluo-aluminate[2]. The former is soluble in water, while the latter is nearly insoluble. The sodium fluoberyllate is converted to beryllium sulphate and purified.

EXPERIMENTAL - SMALL SCALE

IV Crude Material

Beryl

Beryl is the most common mineral that contains enough beryllia to make its extraction practical. It is beryllium aluminum silicate $Be_3Al_2(SiO_3)_6$, and usually contains as impurities iron, a little calcium, magnesium, and occasionally calcium. This mineral is found in appreciable quantities in various parts of the United States.[1,13,18]

Preparation

The beryl used in this investigation came in lumps ranging in color from white to green with blue streaks. It was prepared by crushing first with a sledge hammer, then thru a Blake jaw-crusher, then reduced to about 1/16" by the crushing rolls. The product of this machine was rotated in a pebble mill for several days before it passed a 100 mesh sieve.

Analysis

Beryl has the following composition:-

	By Calculation	By Analysis	
BeO	13.9 o/o	10. o/o	
Al_2O_3	19.0 o/o	19. o/o	
SiO_2	67.1 o/o	65.5 o/o	
Fe_2O_3		1.7	
CaO			Not determined quantitatively
MgO			
H_2O			
	100.0 o/o	96.2 o/o	

V Gibson's Method of Extraction

Experimental

The ammonium hydrogen fluoride used in this process was prepared by neutralizing ammonium carbonate with technical hydrofluoric acid in an iron pot and then adding a portion of hydrofluoric acid equal to the first portion. The solution was concentrated and cooled to allow the product to crystallize. The salt was separated, dried, and kept in wax bottles.

A 50 gram sample of beryl was mixed with 300 grams of ammonium hydrogen fluoride and heated in a 6 inch iron pan on a hot plate. The solidified mass was cooled, ground, and reheated until it had a red color. This was ground and treated with 2 successive 2 liter portions of hot water. The filtered solution was evaporated to a small volume and treated with concentrated sulphuric acid. The solution of sulphates was heated to expel the excess acid. The residue was taken up with water and the solution filtered. After boiling the solution with nitric acid, it was cooled and added in small portions at a time to a solution containing 40 grams of ammonium carbonate.

Since an analysis of the precipitate thrown down here proved the presence of appreciable quantities of beryllium, it was treated with a second portion of ammonium carbonate. The filtrates were combined and treated with mercuric chloride and ammonium sulphide for removal of iron. After filtration, the solution was boiled to precipitate beryllium basic carbonate. However, instead of this granular salt, the flocculent beryllium hydroxide came down. This was filtered, washed, dried and ignited to the oxide.

Results

The process yielded 5 grams of crude beryllium oxide from 50 grams of beryl. The product was grayish white, and gave a lemon yellow solution in hydrochloric acid. It contained 77.5 o/o beryllium oxide and over 4 o/o of the combined oxides of aluminum and iron. The yield of actual BeO therefore was 77.5 o/o of the theoretical.

A rough calculation of the cost of the chemicals required was made as follows:-

1 lb. Ammonium hydrogen fluoride	1.25
1 lb. Sulphuric acid	.08
Ammonium carbonate and miscellaneous	.25
	$1.58

The cost per gram of oxide was therefore $0.41.

Since a large leaden dish was not available for the neutralization of the hydrofluoric acid, that procedure was carried out in an iron pan. The large amount of iron introduced in this manner contaminated the final product. Considerable care had to be exercised to control the fusion temperature so as to obtain the beryllium with as little aluminum as possible. As an aid to the control, the mass was cooled several times and pulverized and reheated.

VI Lebeau's Method of Extraction

Experimental

A 100 gram batch of beryl was mixed with 200 grams of calcium fluoride and heated in a graphite crucible for about an hour and a half in a gas-fired pot furnace at approximately 1000 degrees C. The fused mass was poured into iron molds, and after cooling was granu-

lated. This material was put into an earthenware jar and enough concentrated sulphuric acid added to form a jelly-like mass. External heat was applied when the reaction slowed down, and after the action was complete the mass was poured by small portions into water. The fine precipitate of calcium sulphate formed was filtered off and the filtrate concentrated. The excess acid was neutralized with sodium carbonate, and the solution concentrated. The first material to separate from solution was calcium sulphate. Sodium alum contaminated with calcium and beryllium separated next. A recrystallization left the beryllium in the mother liquor. This was neutralized with ammonium hydroxide and was shaken with a large excess of ammonium carbonate and allowed to stand with occasional shaking for three days. After filtration, the clear solution was treated with a little ammonium sulphide, filtered, and boiled. The beryllium basic carbonate which precipitated, was filtered, washed, dried, and ignited to the oxide.

Results

The product derived from this procedure weighed 5 grams. It had a brown color and contained considerable iron. The yield was 50 o/o of the theoretical; while the cost of chemicals per gram of beryllium oxide was $0.16. This was calculated as follows:-

Calcium fluoride	$0.05
Sulphuric acid	.10
Sodium carbonate	.10
Ammonium carbonate	.35
Ammonium hydroxide	.07
5 gram Beryllium oxide cost	$0.67

The fusion by means of calcium fluoride in a graphite crucible takes place very readily, and the melt is easily broken up. On account of the greater solubility of sodium alum than the potassium alum, it was necessary to concentrate the solution to a point where almost all of the calcium separated as the sulphate. This was in the form of a very fine powder, the filtration of which was very difficult. The sodium alum had to be crystallized several times at a low temperature in order to get a good product. It should be noted that Lebeau does not claim the product of this process to be very pure; but he gives a method for its purification.

VII Pollok's Method of Extraction

Experimental

A 100 gram sample of beryl was fused with an equal amount of sodium hydroxide. The mass was broken up, and to it was added an excess of hydrochloric acid. After allowing the mixture to stand for a day, the silica was filtered off and washed. To the filtrate ammonium hydroxide was added, and the precipitate thus obtained was filtered off and washed, and dissolved in the smallest possible amount of hydrochloric acid. This solution was saturated with hydrochloric acid. This treatment precipitated most of the aluminum as the tetrahydrated aluminum chloride in the form of very pure, pretty, needlelike crystals. The solution was filtered thru glass wool, and the aluminum chloride washed with concentrated hydrochloric acid. Seventy grams of the salt was obtained in this manner.

The filtrate was distilled to half its volume, the liberated hydrogen chloride being absorbed in water for future use. The cooled solution of chlorides was neutralized with ammonium hydroxide and

then slowly added to a saturated solution of ammonium carbonate, which was being stirred constantly. The beryllium passed into solution, leaving the iron and aluminum behind. After allowing the mixture to stand for complete separation of the iron, it was filtered. The precipitate was redissolved in acid, neutralized, and retreated with ammonium carbonate. The combined filtrates were treated with a little ammonium sulphide, filtered, and the filtrate diluted and boiled. Several dilutions and boilings were performed, in each case adding any beryllium basic carbonate to the main precipitate. All of this was ignited to the oxide, the weight of which was 4 grams.

Results

The yield of beryllium oxide was 40 o/o of the theoretical and was of a high degree of purity. The following calculation places the cost of the chemicals necessary for the production of one gram of beryllium oxide at $0.22.

Sodium hydroxide	$0.04
Hydrochloric acid	.64
Sulphuric acid	.16
Ammonium Carbonate	.25
	$1.09
Credit for Aluminum chloride	.20
	$0.89

Cost per gram is $0.22.

For the saturation several devices were tried before the best conditions for the process were obtained. The preparation of the hydrogen chloride by the action of sulphuric acid on salt had to be abandoned because the flow of gas could not be controlled easily

enough. The method adopted was to allow hydrochloric acid to drip into hot sulphuric acid. Various shapes of towers were discarded as being useless for the saturation chamber because the precipitated salt clogged them up, thus creating too large a gas pressure in the system.

The solution to this problem was a series of four 250 cc. wide mouth bottles, connected in series by glass tubing. It was necessary to keep the bottles in beakers containing cold water in order to keep the temperature of the solution low enough to dissolve a large amount of the gas. The gas inlet tube should terminate 1/4" above the surface of the liquid.

Saturation Apparatus

In the accompaning photograph taken before a trap was introduced after the generater and without the cooling apparatus, the range in color of the solution depending on the degree of saturation is clearly shown. In the first bottle, the precipitation is almost complete; while the last one contains a fresh solution. The Erlenmeyer flask seen behind the third bottle contains the saturated solution.

Pollok's process has an advantage in that it is not necessary to evaporate the solution to dryness for the removal of silica. The time required is short, and inasmuch as it offered a rather clean separation of beryllium and aluminum at a low cost, it was tried on a larger scale.

VIII Parsons' Method of Extraction

Experimental

A one hundred gram sample of beryl was fused with an equal weight of caustic soda in a nickel crucible. The fused mass was broken up, sulphuric acid added and the mass heated until the excess of acid was driven off. To the residue hot water was added, and the resulting solution containing the sulphates of beryllium, aluminum, iron, and sodium was evaporated until the sodium alum separated. The mother liquor was boiled with nitric acid to oxidize the iron, neutralized with ammonium hydroxide, and enough sodium bicarbonate added to saturate the solution. The mixture was warmed and shaken at intervals for 24 hours. The solution was filtered, the residue dissolved and retreated. A little ammonium sulphide was added to the combined filtrates, the precipitate removed, and the solution diluted to 5 times its volume. On heating the solution to the boiling point by means of live steam, beryllium basic carbonate precipitated. This was filtered, washed, dried, and ignited to the oxide.

Results

The yield of oxide was 7 grams or 70 o/o of the theoretical. The material had a fine white color, and was comparatively free of impurities especially iron. Material made in this manner contains not

able quantities of occluded sodium salts[14].

The cost per gram for the chemicals used was found by the following approximation to be $0.06.

Sodium hydroxide	$0.04
Sulphuric acid	.16
Ammonia, nitric acid, etc.	.14
Sodium bicarbonate	.06
Cost for total chemicals	$0.40

During this run, it became apparent that the details of the original process had to be followed very closely to get any kind of results. In view of the high cost of potassium hydroxide, it seemed advisable to make the fusion with the corresponding sodium salt. There is a serious disadvantage, however, in the fact that the higher solubility of sodium alum leaves a very large amount of aluminum to be removed by the sodium bicarbonate treatment.

This process is of especial value because it requires cheap chemicals, no special apparatus, the yield is good, and the product is of a good degree of purity.

IX Copaux' Method of Extraction

Experimental

A one hundred gram sample of beryl was mixed with two hundred grams of sodium fluosilicate and heated in a fire clay crucible at 1000 degrees C. for about 45 minutes. The fritted mass was broken up and treated with hot water in order to extract the sodium fluoberyllate. To this solution ammonium hydroxide was added, and the hydroxides of beryllium, aluminum and iron were filtered off and redissolved in sulphuric acid. This solution was concentrated to sep-

arate beryllium sulphate, which was purified by means of ammonium carbonate in the usual manner.

Results

The yield of beryllium oxide obtained in this manner was 3.5 grams or 35 o/o. The product had a dark color and contained considerable aluminum and iron.

The determination of the cost of the material follows:-

Sodium fluosilicate	$0.45
Ammonium hydroxide	.14
Sulphuric acid	.08
Ammonium carbonate, etc.	.25
Cost for total product	$0.92

The cost per gram of oxide was therefore $0.26.

The sodium fluosilicate had to be prepared. This was done by heating in a flask a mixture of calcium fluoride, sand, and sulphuric acid. The silicon fluoride that is evolved is absorbed in a sodium hydroxide solution to give silicic acid and sodium fluosilicate. The solution is filtered to remove the silicic acid, and the filtrate evaporated to obtain the crystals of sodium fluosilicate. This preparation in the laboratory was an unpleasant and dangerous process as the materials are very corrosive.

This process for the decomposition of beryl was not very successful. The action on the crucible decreased the yield considerably. The separation of the beryllium from aluminum is not as sharp as could be expected.

The method is said to have been applied on a commercial scale, a factor which helps explain the lack of details in the literature.

X Choice of Methods for Large Scale Extraction

Gibson's method was eliminated because it required large amounts of a very expensive and dangerous chemical. For the successful application of this process considerable platinum ware would be required.

Lebeau's method was not tried because of the complications arising from the calcium salt, and because of the difficulty in removing large quantities of aluminum as sodium alum. A very serious objection is the fact that the impure oxide would have to be purified by a process that would raise the cost of the product considerably.

The method of Copaux was eliminated because it is expensive, and generally unsuited for laboratory work.

The reasons for choosing Pollok'c method for investigation on a large scale were:-

1. There were few operations.
2. The product was rather pure.
3. The time required was reasonable.
4. The results indicated the possibility of a substantial decrease in cost on a larger scale.
5. It seemed possible to design simple apparatus to insure successful operation.

Parsons' method was also chosen for the following reasons:-

1. The operations were simple.
2. The product was of good quality.
3. The process was short.
4. The cost per unit of beryllia was low.
5. No special apparatus was required.

EXPERIMENTAL - LARGE SCALE

XI Pollok's Method of Extraction

Experimental

Since a graphite crucible large enough to hold 1 kilogram each of beryl and sodium hydroxide could not be obtained, the mixture was placed in a Sagger box (shallow fire-clay box) and heated in a reverberatory furnace for 2 hours at a temperature just below the fusion point. The mass taken from the box weighed 1.73 kilograms. This was ground very fine, but by so doing a considerable quantity of iron was introduced. To the powder in a 4 gallon earthenware jar 7 pounds of hydrochloric acid was added, and the mixture stirred well. Two liters of water were added and the jar placed in a "Parr Evaporating Box" and heated. After allowing the mixture to cool and settle, the clear solution was siphoned off. This process was repeated 4 times before all the beryllium was extracted from the mixture. The total amount of acid used was 15 pounds, and the total volume of solution was 30 liters. This solution was evaporated to about half its volume, and to it was added enough ammonium hydroxide to precipitate all the aluminum, beryllium, and iron.

The gelatinous nature of the precipitate was such that in trying to filter the solution thru a Buchner funnel into a 4 liter flask it clogged up the paper so badly that the flask collapsed. Filtration by gravity was impossible. It was next tried to filter the slurry by means of a small hand-operated German Filter Press, but this method was a failure. The Sperry Filter Press was then tried under varying conditions such as temperature of solution and thickness of

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filter cloth. No results were obtained with this machine, as a considerable quantity of solid went thru the filter, and because the machine clogged up after a very thin cake had formed. It was impractical to open the press as soon as a small cake had formed, because the latter still contained so much liquid that it had to be centrifuged.

Vacuum Filter Leaf.

Elaborating on the idea described by Faber[5] and on the principle of the "Moore Vacuum Filter", a filtering device that suited the requirements was constructed. A piece of 1/2 inch galvanized iron pipe was bent to form a frame 6 inches square. One end of the pipe was bent at a right angle to the plane of the frame and cut off so as to leave a 3 inch projection. The wall of the pipe that formed the closed part of the frame was perforated every inch with a 1/16 inch hole. After fitting 2 thin stips of wood across the inside of the frame, the whole frame was covered with pre-shrunk filtering canvass. This was sewn on to form a taunt fitting cover; the strips of wood preventing the two sides from touching when the vacuum is created on the inside. A length of pressure tubing connects the 3 inch projection to a filter flask connected with a suction pump. This device makes a very efficient filter having 72 square inches of filtering area.

The operation of this device is very simple. The suction is applied and the leaf is submerged in the slurry. The liquid passes into the flask; and when a quarter inch cake has formed on each side of the leaf, the apparatus is raised out of the liquid. When the cake has been sucked dry, the leaf is placed in a dish of water, and

the water is pulled thru the cake to wash it. The vacuum is allowed to act until the cake is dry, when a momentary blast of compressed air blown back into the leaf, loosens the solid from the cloth. By means of this device, 12 liters of the slurry contained in a 4 gallon jar was filtered very satisfactorily in a total time of 2 hours.

The precipitate of the hydroxides of aluminum, beryllium, and iron filtered in this manner was dissolved in the smallest possible amount of hydrochloric acid. Due to the volume of solution (3 liters) it was deemed advisable to carry out the absorption of hydrogen chloride in larger apparatus than used on the small scale. Accordingly various size bottles up to 2 liter capacity were tried, but on account of the difficulty in keeping the solution agitated and cool, it was necessary to resort to 250 cc. bottles. This lengthened the process considerably.

After filtration of the aluminum chloride, the solution was heated and the excess hydrogen chloride recovered. The concentrated solution having a volume of 2 liters was neutralized with 300 cc. of ammonium hydroxide. To the saturated solution of ammonium carbonate, which was being agitated by means of a mechanical stirrer, the solution of chlorides was added. After stirring for an hour, the solution was filtered with the vacuum filter leaf described. The precipitate was retreated with 500 grams of ammonium carbonate and the filtrates combined. About 15 cc. of ammonium sulphide was added to precipitate iron, zinc, etc. After removal of this precipitate by filtration, the solution which had a blue color was analyzed and found to contain copper.

Two 50 cc. portions were taken. One was treated with enough ammonium sulphide to remove all the color, and the other received no treatment. These samples were heated, and the beryllium basic carbonate was filtered, washed and ignited. The sample from which no copper was removed gave a larger yield of purer beryllium oxide.

In view of these results, the main portion of the solution was heated directly in a 8 liter Pyrex flask on a steam cone for one hour. The white crystalline precipitate of basic carbonate was filtered off and the solution reheated. This was repeated several times; the product of each heating - which was lower in its carbon dioxide content - being added to the first precipitate.

The beryllium basic carbonate was washed, dried, and ignited to the oxide.

Results

The yield of beryllium oxide was 20 grams or 20 o/o of the theoretical. This could be increased considerably in a run where frequent analyses and experiments did not take so much solution.

The cost for the chemicals required in this process was calculated as follows:-

2.5 lbs. Sodium hydroxide	$0.25
30 lbs. Hydrochloric acid	2.40
1.5 lbs. Ammonium hydroxide	.20
2.5 Ammonium carbonate	1.00
Total cost	$3.85

The cost per gram of beryllium oxide was $0.19.

Even though the yield of oxide was low, the cost per gram by this method was considerably lower on a large scale than on a small scale.

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After a good method of filtration was found, considerable time and effort were saved. The most serious obstacle encountered in this process was the absorption of hydrogen chloride. Development of suitable apparatus for this process on a larger scale might make Pollok's method very satisfactory for commercial application.

XII Parsons' Method of Extraction

Experimental

A kilogram of beryl was mixed with an equal amount of technical sodium hydroxide. Since no crucible large enough to hold this quantity was available, the mixture was put into a semispherical iron pan about 10 inches in diameter and 1/16" thick. This was heated over a gas-fired crucible furnace for 3 hours without effecting a fusion. The only result was the burning of the iron, and the consequent contamination of the mixture.

In order to lower the fusion temperature, about 25 grams of calcium fluoride was added; and half of the mixture at a time was heated in a large (8" x 5") fireclay crucible. The fusion took place at about 1000 degrees C.; and the melt was poured into iron molds, cooled, and crushed. In order to eliminate in the final comparison the losses that took place in the pan and by the attack of the crucible, only 1500 grams of the powder were carried thru the process.

The powdered melt was covered with water in a large evaporating dish and treated with 1 liter of sulphuric acid. The mass was evaporated to dryness, more water and 100 cc. of sulphuric acid added, and again evaporated. A third evaporation with 200 cc. of sulphuric acid was thought to be sufficient.

The treatment of the dried powder with successive portions of hot

water extracted most of the salts and left the silica behind. The total volume of the solution was 10 liters. It had a green color due to the large amount of iron. The excess of acid in this solution was neutralized with sodium carbonate, and the solution concentrated to crystallize sodium alum.

This was not as simple a matter as was expected because of the complexity of the system. After many trials the solution was concentrated until a very large precipitate came down. This was a mixture of several salts; but on heating with a limited amount of water, all but the calcium sulphate dissolved. After removal of that compound, the solution was concentrated until a pale green precipitate came down. This was mostly ferrous sulphate; while the sodium, alumunum, beryllium, and some iron remained in solution. Various temperatures and concentrations were tried before the aluminum was finally separated as aluminum sodium sulphate. The exact conditions could not readily be determined.

The mother liquor from these crystallizations contained all the beryllium, and some aluminum and iron. It was boiled with nitric acid, neutralized with ammonium hydroxide, and to it was added in small portions 300 grams of recrystallized sodium carbonate. The mixture was warmed and shaken occasionally during 24 hours. After cooling, filtering, and retreating the precipitate with another 300 gram portion of sddium bicarbonate, the filtrates were combined. After removing the iron with ammonium sulphide, the solution was diluted to five times its volume and boiled with live steam. Beryllium precipitated as basic carbonate, but the small quantities of carbon dioxide it contained helped only a little in preventing a

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flocculent precipitate. This was filtered off, washed, dried, and ignited to the oxide.

Results

The yield of beryllium oxide was 15 grams from a 750 gram sample of beryl, or 20 o/o of the theoretical. The product was white and was very pure.

Although there are some difficulties in this process on a large scale, it worked very well. A great deal of the difficulty and of the poor yield was due to the substitution of sodium hydroxide for the corresponding potassium compound. Assuming an equal efficiency if the potassium hydroxide was used, a calculation showed that the change would make the cost per gram of product $0.09. The experiment showed that the cost of chemicals for every gram of beryllium oxide was $0.08. This was calculated as follows:-

1.5 lbs. Sodium hydroxide	$0.25
0.5 lb. Calcium floride	.05
3. lbs. Sulphuric acid	.24
0.5 lb. Sodium carbonate and mis.	.24
1.5 lbs. Sodium bicarbonate	.31
Total cost	$1.19

CONCLUSIONS

VIII Suggested Method for Future Investigation

The writer feels that several of the methods could be combined to give one process that would be better than any of those tried. The following method seems worth trying.

The beryl should be fused in a graphite or duriron crucible with calcium fluoride, pulverized, and dissolved in sulphuric acid and evaporated to that concentration at which the calcium sulphate is least soluble. After filtration of most of that compound, the solution should be evaporated to dryness to dehydrate the silica. Since the remaining calcium would cause complications if the solution were concentrated for crystallization of either sodium or potassium alum, it seems advisable to use Pollok's method for the removal of the large bulk of aluminum. The remainder could be separated as in Parson's method by sodium bicarbonate.

XIV Summary

Five different methods were studied for the extraction of beryllium oxide from beryl:

1. From a very small sample, Gibson's method gave a 77.5 o/o yield of beryllium oxide that was not very pure. For every gram of product obtained, the cost for the chemicals amounted to $0.41. The nature of the reagents would indicate that the process would work well on a very small scale or on a commercial scale, but not on a large laboratory scale.

2. Beryllium oxide prepared by Lebeau's method was of poor quality even though not very expensive. A 50 o/o yield was obtained at a

cost for chemicals of \$0.16 per gram of oxide. The apparent economy in chemicals was counterbalanced by the time and trouble involved. The use of potassium instead of sodium for the separation of aluminum as alum would probably make this process applicable for laboratory work.

3. Pollok's method on the small scale gave a 40 o/o yield of beryllium oxide at a cost of \$0.22 per gram. On the larger scale, the yield was only 20 o/o, but the cost was reduced to \$0.19. The product of both trials was very pure. After several runs on a large scale, the yield could probably be increased considerably.

4. Beryllium oxide prepared by Parsons' method was practically free of aluminum and iron but contained sodium. Although the yields were 40 o/o and 20 o/o in the small and large scale respectively, the cost for chemicals per gram of product remained low - \$0.06 and \$0.08. This process is best suited for a 1 kilogram batch of beryl, but the large volume of solutions would be disadvantageous on a larger scale. Of all the methods tried, this was the best because no special apparatus was required, the product was pure, and the process was simple.

5. Copaux' method was not very successful in the laboratory. A 35 o/o of beryllium oxide was obtained at a cost of \$0.26 per gram. In a plant where apparatus built of special material were at hand, the process would probably be quite successful.

A method has been suggested for future investigation.

A filtering device has been designed and constructed and its efficiency proven.

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